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(54) Title: CHAIN EXTENDED DENDRITIC POLYETHER

(57) Abstract: A chain extended dendritic polyether comprising a dendritic core polymer and a chain extension bonded to said core polymer, which chain extended dendritic polyether optionally is at least partially chain terminated and/or partially functionalised. The core polymer is a polyhydric dendritic polyether and the chain extension is obtained by addition of at least one alkylene oxide to at least one hydroxyl group in said core polymer.

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## CHAIN EXTENDED DENDRITIC POLYETHER

The present invention refers to a chain extended dendritic polyether comprising a polyhydric dendritic core polymer and chain extension bonded to said core polymer, which chain extended dendritic polyether optionally is at least partially chain terminated and/or functionalised. Said chain extension is obtained by addition of at least one alkylene oxide. In a further aspect, the present invention refers to a composition comprising the subject chain extended dendritic polyether and in yet a further aspect to the use of the same.

Compounds with a highly branched, treelike, molecular structure have been known for a long time. Dendritic polymers belong to a group of polymers characterised by densely branched structures and a large number of end groups. They are obtained by for instance polymerisation of  $AB_x$  monomers, typically  $AB_2$  monomers, giving branched structures with an exponential growth in both molecular weight and end group functionality as a function of the degree of polymerisation. Polymers designated as dendritic, or sometimes hyperbranched, may to a certain degree hold an asymmetry, yet maintaining the highly branched treelike structure. Dendrimers generally are highly symmetric. Dendrimers can be said to be monodisperse species of dendritic polymers. Dendritic polymers normally consist of an initiator, core or nucleus having one or more reactive sites and a number of branching layers and, optionally, a layer of chain terminating molecules. The layers are usually called generations and the branches dendrons, which are designations herein used. It is well known that the globular structures obtained with dendritic polymers allow for excellent flow and processing properties at high molecular weights. The exceptional concentration of reactive groups allows for rapid curing in thermosetting applications and provide unique possibilities to customise properties in a wide range of different end-uses.

Literature discussing various highly branched and dendritic molecules and macromolecule include:

- "*Polybenzyl Type Polymers*", by Howard C. Haas et al published in *J. Polymer Sci.* vol. XV (1955) pp. 503-515, wherein non-randomly substituted highly branched benzyl type polymers are synthesized and analysed.
- "*Strukturuntersuchungen an Sternmolekülen mit Glykogen als Kern*", by Walther Burchard et al published in *Makromolekulare Chemie*, 150 (1971) pp. 63-71, wherein the structure of molecules having treelike amylose chains and a glycogen core are disclosed.
- "*Statistical Mechanism of Random Coil Networks*" and "*Elasticity and Chain Dimensions in Gaussian Networks*", by William W. Graessley published in *Macromolecules*, vol. 8 no. 2 (1975) pp. 186-190 and vol. 8 no. 6 (1975) pp 865-868, wherein molecules comprising tri and tetrafunctional central cores (initiators) and concentrically treelike (dendritic) branches are disclosed. The term micronetworks is introduced to describe these molecules.

- "Static and Dynamic Scattering Behavior of Regularly Branched Chains: A Model of Soft-Sphere Microgels", by Walther Burchard et al published in *J. Polymer Sci. Polym. Phys. Ed.*, vol. 20 (1982) pp. 157-171, wherein is disclosed, among other models, the theory behind a molecular model comprising a trifunctional core being symmetrically branched whereby continued branch replication yields increased branch multiplicity and an increased number of terminal groups.

Various dendritic materials have during the last one or two decades attracted general attention. Patents, patent applications and other works issued or published during the last decades are summarised by for instance H. Galina et al in *Polymery*; English translation in *Int. Polym. Sci. Tech.*, 1995, 22, 70. The state of the art is excellently compiled in for instance "*Dendritic Molecules · Concepts · Syntheses · Perspective*" by G.R. Newkome, C.N. Moorefield and F. Vögtle - VCH Verlagsgesellschaft mbH, 1996.

A number of patents and patent applications disclosing various dendritic polymers and processes for synthesis thereof have for various types of products been issued or published and include EP 0 115 771, SE 468 771, WO 93/18075, EP 0 575 596, SE 503 342, US 5,561,214, WO 00/56802.

EP 0 115 771 claims a dense star polymer having at least three symmetrical core branches, each core branch having at least one terminal group, and a ratio terminal groups to core branches being greater than 2:1. The properties of claimed polymer is specified through a comparative relation to an unspecified star polymer. EP 0 115 771 also relates to a process, which process substantially also is disclosed in US 4,410,688, for synthesis of a symmetrical dense star polymer. The process teaches a repeated and alternately addition of alkyl acrylate and alkylene diamine to a core consisting of ammonia.

SE 468 771 discloses a dendritic macromolecule substantially built up from polyester units and a process for synthesis of said macromolecule. The macromolecule is composed of an initiator, having at least one hydroxyl group, to which initiator at least one branching generation comprising at least one chain extender, having at least one carboxyl group and at least two hydroxyl groups, is added. The macromolecule is optionally chain terminated. The process for synthesis of said macromolecule teaches a co-esterification of the initiator and the chain extender, optionally followed by a chain termination. The process yields inexpensive polydisperse dendritic macromolecules.

WO 93/18075 teaches a hyperbranched polymer having at least six terminal hydroxyl or carboxyl groups and a process for its synthesis. The hyperbranched polymer is synthesized by

repeated and alternately addition of a compound having at least one anhydride group followed by a compound having at least one epoxide group to a core having at least one hydroxyl group.

EP 0 575 596 discloses a dendritic macromolecule comprising a core having 1-10 functional groups and branches synthesized from vinyl cyanide units as well as a process for synthesis thereof. The process involves three repeated steps beginning with reaction between the core and monomeric vinyl cyanide units followed by reduction of incorporated nitrile groups to amine groups. In a third step said amine groups are reacted with monomeric vinyl cyanide units.

SE 503 342 discloses a dendritic macromolecule of polyester type and a process for synthesis of said macromolecule. The macromolecule substantially is composed of a core, having at least one epoxide group, to which core at least one branching generation comprising at least one chain extender, having at least three reactive functions of which at least one is a carboxyl or epoxide group and at least one is a hydroxyl group, is added. The macromolecule is optionally chain terminated. The process teaches self condensation of the chain extender molecules yielding a dendron (a core branch), which dendron in a second step is added to the core. The process also comprises an optional further chain extension by addition of spacing or branching chain extenders and/or an optional chain termination. The process yields inexpensive polydisperse dendritic macromolecules.

WO 00/56802 discloses dendritic polyethers obtained by ring opening polymerisation of oxetanes, optionally in the presence of a core molecule. The polyethers are optionally further processed such as chain extended, chain terminated and/or functionalised by reaction with compounds such as hydroxyfunctional carboxylic acids, lactones, carboxylic acids, haloperoxyacids, isocyanates, allylhalides and epihalohydrins.

Dendritic polyethers made by ring opening polymerisation have attracted some interest recently. Both dendritic structures made from glycidol and 3-ethyl-3-hydroxymethyl oxetane have been studied and published by *inter alia* E.J. Vandenberg, *Pol. Sci., Part A: Polym. Chem.*, 1989, 27, 3113, A. Sunder et.al., *Macromolecules*, 1999, 32, 4240, and H. Magnusson et.al. *Macromol. Rapid Commun.*, 1999, 20, 453-457.

Dendritic polyethers obtained by ring opening polymerisation offer a rapid process for obtaining dendritic structures. Dendritic polyethers are furthermore hydrolytically stable, which is of interest for applications wherein an aqueous and/or alkaline environment is employed.

It is of particular interest to study dendritic polyethers made by ring opening polymerisation of 3-ethyl-3-hydroxymethyl oxetane (trimethylolpropane oxetane, TMPO), since the monomer is non-toxic and hence environmentally friendly. The TMPO monomer is, furthermore, only possible to polymerise under cationic conditions, which allows the hydroxyl functionality to be modified under alkaline conditions prior to polymerisation. Said modified product can then be used as co-monomer with neat TMPO and specific functionalities can thereby be incorporated in the inherent dendritic polymer backbone. Dendritic polymers made from TMPO offer interesting physical properties such as a glass transition temperature ( $T_g$ ) in the range of 40°C, yet low melt viscosity at elevated temperatures. They are also as previously disclosed hydrolytically stable and can be used in strongly alkaline environments.

It has now been found that it is possible, in spite of the high functionality and molecular weight, to use hydroxyfunctional dendritic polyethers as core molecules which through anionic ring opening are linearly extended with cyclic ethers of oxirane type, whereby chain extended dendritic polyethers with terminal hydroxyl groups and narrow molecular weight distribution are obtained.

The present invention accordingly refers to novel chain extended dendritic polyether comprising a dendritic core polymer and a substantially linear chain extension bonded to said core polymer. The chain extended dendritic polyether may optionally be at least partially chain terminated and/or functionalised. The core polymer is a polyhydric dendritic polyether and the chain extension is obtained by addition of at least one alkylene oxide to at least one hydroxyl group in said core polymer. The preferred molar ratio said core polymer to said alkylene oxide is between 1:1 and 1:100, such as between 1:2 and 1:50. The novel dendritic polymer of the present invention useful as a product *per se* or as component, raw material, in the manufacture of a large number of resinous and polymeric products.

The chain extended dendritic polyether according to the present invention has exceptionally low viscosity with regard to its molecular weight. Obtained viscosity range is regarded as being the lowest values reported for any polydisperse dendritic polymer at a given molecular weight and hydroxyl functionality. The chain extended dendritic polyether according to the present invention has, furthermore, an inherently flexible backbone promoting good flexibility and adhesion to coatings as well as thermoset resins. The high end group functionality provides, at the same time excellent film hardness and modulus retention to coatings and thermoset resins. The chain extended dendritic polyether according to the present invention provides a unique amphiphilic character. Obtained linear alkylene oxide chains will, when using for instance ethylene oxide as chain extending monomer, since they are hydrophilic provide inherent surfactant and stabilising properties. The high end group functionality of the chain extended dendritic polyethers according to the present invention, allows for chain

stoppers of hydrophobic nature, such as aliphatic mono isocyanates or carboxylic acids, to be used to provide the dendritic polyether with an amphiphilic nature. The amphiphilic products obtained have unexpectedly been found to be exceptionally effective as dispersing agents for pigments and as dispersing resins for alkyds, polyesters, polyurethanes and polymer dispersions obtained by emulsion polymerisation. Dispersing products are obtained when unsaturated carboxylic acids, such as sunflower fatty acid, tall oil fatty acid or linseed fatty acid, are used, which dispersing products when mixed with dryers will contribute to crosslinking of formed films. Coatings with good rheological properties and excellent final film properties can hence be obtained without the use of solvents, coalescent agents and/or conventional surfactants. Radiation curing polymers with high functionality, high molecular weight and low viscosity are obtained when unsaturated carboxylic acids, such as acrylic and maleic acids, are used.

The alkylene oxide providing the substantially linear chain extension is in preferred embodiments of the present invention ethylene oxide, propylene oxide, 1,3-butylene oxide, 2,4-butylene oxide, cyclohexene oxide, butadiene monoxide, phenylethylene oxide or a mixture of two or more of said alkylene oxides.

The polyhydric dendritic polyether, used as core polymer according to the present invention, is preferably obtained by ring opening addition of at least one oxetane to a di, tri or polyhydric core molecule at a molar ratio yielding a polyhydric dendritic polyether comprising a core molecule and at least one branching generation bonded to at least one hydroxyl group in said di, tri or polyhydric core molecule. The di, tri or polyhydric core molecule is in preferred embodiments of the polyhydric dendritic polyether a di, tri or polyhydric alcohol or a reaction product between at least one alkylene oxide, such as ethylene oxide, propylene oxide, 1,3-butylene oxide, 2,4-butylene oxide, cyclohexene oxide, butadiene monoxide and/or phenylethylene oxide, and a di, tri or polyhydric alcohol. Said di, tri or polyhydric alcohol is suitably selected from the group consisting of 1, $\omega$ -diols, 5-hydroxy-1,3-dioxanes, 5-hydroxyalkyl-1,3-dioxanes, 5-alkyl-5-hydroxyalkyl-1,3-dioxanes, 5,5-di(hydroxyalkyl)-1,3-dioxanes, 2-alkyl-1,3-propanediols, 2,2-dialkyl-1,3-propanediols, 2-hydroxy-1,3-propanediols, 2-hydroxy-2-alkyl-1,3-propanediols, 2-hydroxyalkyl-2-alkyl-1,3-propanediols, 2,2-di(hydroxyalkyl)1,3-propanediols and dimers, trimers or polymers of said di, tri or polyhydric alcohols. Alkyl is here preferably C<sub>1</sub>-C<sub>24</sub>, such as C<sub>1</sub>-C<sub>12</sub> or C<sub>1</sub>-C<sub>8</sub> alkanyl or alkenyl.

Various embodiments of the polyhydric dendritic polyether include especially preferred embodiments wherein the di, tri or polyhydric core molecule is 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,6-cyclohexanedimethanol, 5,5-dihydroxymethyl-1,3-dioxane, 2-methyl-1,3-propanediol, 2-methyl-2-ethyl-1,3-propanediol, 2-ethyl-2-butyl-1,3-

-propanediol, neopentyl glycol, dimethylolethane, trimethylolpropane, 1,1-dimethylolcyclohexane, glycerol, trimethylolethane, trimethylolpropane, diglycerol, ditrimethylolethane, ditrimethylolpropane, pentaerythritol, dipentaerythritol, anhydroenneaheptitol, sorbitol, mannitol or a reaction between a previously disclosed alkylene oxide and a herein disclosed alcohol.

The oxetane providing said at least one branching generation is preferably and advantageously a 3-alkyl-3-(hydroxyalkyl)oxetane, a 3,3-di(hydroxyalkyl)oxetane, a 3-alkyl-3-(hydroxyalkoxy)oxetane, a 3-alkyl-3-(hydroxyalkoxyalkyl)oxetane or a dimer, trimer or polymer of a 3-alkyl-3-(hydroxyalkyl)oxetane, a 3,3-di(hydroxyalkyl)oxetane, a 3-alkyl-3-(hydroxyalkoxy)-oxetane or a 3-alkyl-3-(hydroxyalkoxyalkyl)oxetane. Alkyl is here preferably C<sub>1</sub>-C<sub>24</sub>, such as C<sub>1</sub>-C<sub>12</sub> or C<sub>1</sub>-C<sub>8</sub> alkanyl or alkenyl and alkoxy comprises preferably 1-50, such as 2-20, alkoxy units derived from at least one alkylene oxide, such as ethylene oxide, propylene oxide, 1,3-butylene oxide, 2,4-butylene oxide, cyclohexene oxide, butadiene monoxide, phenylethylene oxide or a mixture of two or more of said alkylene oxides. Said oxetane is most preferably an oxetane of trimethylolethane, trimethylolpropane, pentaerythritol, ditrimethylolethane, ditrimethylolpropane or dipentaerythritol, such as 3-methyl-3-(hydroxymethyl)oxetane, 3-ethyl-3-(hydroxymethyl)oxetane and/or 3,3-di(hydroxymethyl)oxetane.

The chain extended dendritic polyether of the present invention is suitably at least partially chain terminated by addition to said chain extension and/or said core polymer of at least one aliphatic or aromatic saturated or unsaturated carboxylic acid or a corresponding anhydride or halide, at least one hydroxyfunctional carboxylic acid, such as 2,2-bis(hydroxymethyl)propanoic acid, 2,2-bis(hydroxymethyl)butanoic acid, 2,2-bis(hydroxymethyl)pentanoic acid, 2,3-dihydroxy- propanoic acid, hydroxypentanoic acid, hydroxypropanoic acid and/or 2,2-dimethyl- -3-hydroxypropanoic acid, at least one lactone, such as  $\beta$ -propiolactone,  $\gamma$ -butyrolactone,  $\delta$ -valerolactone,  $\epsilon$ -caprolactone and/or  $\zeta$ -enantholactone, at least one aliphatic or aromatic mono or diisocyanate, such as toluene-2,4-diisocyanate, toluene-2,6-diisocyanate, hexamethylene diisocyanate and/or isophorone diisocyanate, at least one epoxidised saturated or unsaturated alcohol, such as a C<sub>5</sub>-C<sub>24</sub> alkanol or alkenol, at least one allyl or vinyl ether, at least one thiol, at least one glycidyl ether, and/or at least one sulphonate or phosphate, and/or is at least partially functionalised by reaction with at least haloperoxy acid or anhydride, such as peroxyformic acid, peroxyacetic acid, peroxybenzoic acid, m-chloroperoxybenzoic acid and/or trifluoroperoxyacetic acid, at least one allylhalide, such as allylbromide and/or allylchloride, and/or at least one epihalohydrin, such as epichlorohydrin or epibromohydrin.

Said at least one aliphatic or aromatic carboxylic acid is suitably acetic acid, propionic acid, butyric acid, valeric acid, isobutyric acid, trimethylacetic acid, 2-ethylhexanoic acid, nonanoic acid, isononanoic acid, heptanoic acid, caproic acid, caprylic acid, capric acid, benzoic acid,

para-tert.butylbenzoic acid, pelargonic acid, lauric acid, myristic acid, palmitic acid, stearic acid, isostearic acid, behenic acid, lignoceric acid, cerotic acid, montanoic acid, abietic acid, sorbinic acid, oleic acid, ricinoleic acid, linoleic acid, linolenic acid, erucic acid, soybean fatty acid, linseed fatty acid, dehydrated castor fatty acid, tall oil fatty acid, tung oil fatty acid, sunflower fatty acid, safflower fatty acid, *o*-phthalic acid, isophthalic acid, terephthalic acid, azeleic acid, adipic acid and/or trimellitic acid or, where applicable, a to a said acid corresponding anhydride.

Said at least one carboxylic acid is furthermore preferably acrylic acid, methacrylic acid, crotonic acid, isocrotonic acid or a to a said acid corresponding anhydride or halide, and/or maleic anhydride or fumaric acid. Said at least partial chain termination confers, when performed by addition of at least one of said preferred acids, properties possible to utilise in for instance radiation curing coatings and inks.

The present invention refers in a further aspect to a composition comprising the chain extended dendritic polyether disclosed above in an amount of at least 0.1%, such as 0.5-80%, 0.5-50% or 1-25%, by weight.

Various embodiments of the chain extended dendritic polyether of the present invention are suitably and advantageously used as or utilised in preparation of air drying alkyd resins, 1- and 2-component polyurethane coatings and adhesives, saturated and unsaturated polyesters, toughening agents for thermosetting resins, such as epoxy resins, unsaturated polyesters, vinyl esters, polyurethanes, maleimides, cyanate esters, phenolics, urea-formaldehyde resins and melamine-formaldehyde resins as well as composites made therefrom, pigment dispersion agents for solvent-free, solventborne and waterborne coatings, water dispersible resins for alkyd emulsions, acrylic dispersions and polyurethane dispersions, dispersing polymers or resins, such as reactive polymeric surfactants, for non-amphiphilic alkyds, polyesters, polyethers and polyurethanes, processing aids for polyolefines and thermoplastics, such as polycarbonates, polyesters, polyamides, polyimides and polyurethanes, concrete admixtures imparting for instance fluidity to hydraulic compositions, such as cement pastes, mortars and concretes, and/or radiation curing coatings, printing inks and adhesives.

Without further elaboration, it is believed that one skilled in the art can, using the preceding description, utilize the present invention to its fullest extent. The following preferred specific embodiments are, therefore, to be construed as merely illustrative and not limitative of the remainder of the disclosure in any way whatsoever. These and other objects and the attendant advantages will be more fully understood from the following detailed description, taken in conjunction with appended embodiment Examples 1-19 illustrating:

Examples 1 and 2: Preparation of second and third generation dendritic polyethers used in Example 3-6 as core polymers.

Examples 3 and 4: Preparation of chain extended dendritic polyethers in accordance with embodiments of the present invention. The product of Example 1 is used as core polymer and ethylene oxide as chain extension monomer.

Examples 5 and 6: Preparation of chain extended dendritic polyethers in accordance with embodiments of the present invention. The product of Example 2 is used as core polymer and ethylene oxide as chain extension monomer.

Example 7 and 8: Chain termination, in accordance with embodiments of the present invention, of the chain extended dendritic polyethers of Examples 3 and 5. Acrylic acid is used as chain termination monomer.

Example 9: Chain termination, in accordance with an embodiment of the present invention, of the chain extended dendritic polyether of Example 4. Sunflower fatty acid is used as chain termination monomer.

Example 10 and 11: Evaluation in radiation curing coatings of the products obtained in Examples 7 and 8.

Example 12: Evaluation as toughener in anhydride cured epoxy resin of the products obtained in Example 5.

Example 13-18: Preparation of waterborne systems using the product obtained in Example 9.

Example 19: Evaluation of waterborne systems obtained in Examples 14-18.

### **Example 1**

7.28 kg of ethoxylated pentaerythritol (Polyol PP50<sup>TM</sup>, Perstorp Specialty Chemicals AB) and 71.7 g of BF<sub>3</sub> ethyl etherate were charged to a steel reactor equipped with stirrer, oil heating, water cooling, nitrogen inlet and cooler. The mixture was heated to 110°C. Forced cooling was imposed to the reactor and addition of 28.55 kg of a 3-ethyl-3-(hydroxymethyl)oxetane (TMPO) commenced at a feeding rate of 0.82 kgm<sup>-1</sup>. The reaction was exothermic and the exotherm continued for a further 20 minutes after completed feeding of TMPO and excessive cooling was required. The reaction was then allowed to continue at 110°C for a further 4 hours after which 125 g of aqueous NaOH (41%) was added to stop the living character of the polymer. The reaction mixture was stirred for 20 minutes at 110°C and full vacuum was then applied to remove any residual monomer and water originating from the aqueous base.

Obtained polyhydric dendritic polyether of two generations exhibited following properties:

Hydroxyl value, mg KOH/g:	518
Molecular weight, (GPC) g/mole:	1450
Nominal molecular weight, (GPC) g/mole:	1088
Polydispersity index:	1.33

### Example 2

3.64 kg of ethoxylated pentaerythritol (Polyol PP50™, Perstorp Specialty Chemicals AB) and 73.7 g of  $\text{BF}_3$  ethyl etherate were charged to a steel reactor equipped with stirrer, oil heating, water cooling, nitrogen inlet and cooler. The mixture was heated to 110°C. Forced cooling was imposed to the reactor and addition of 33.2 kg of a 3-ethyl-3-(hydroxymethyl)oxetane (TMPO) commenced at a feeding rate of 0.82  $\text{kg m}^{-1}$ . The reaction was exothermic and the exotherm continued for a further 20 minutes after completed feeding of TMPO and excessive cooling was required. The reaction was then allowed to continue at 110°C for a further 4 hours after which 405 g of aqueous NaOH (41%) was added to stop the living character of the polymer. The reaction mixture was stirred for 20 minutes at 110°C and full vacuum was then applied to remove any residual monomer and water originating from the aqueous base.

Obtained polyhydric dendritic polyether of three generations exhibited following properties:

Hydroxyl value, mg KOH/g:	496
Molecular weight, (GPC) g/mole:	3006
Nominal molecular weight, (GPC) g/mole:	2362
Polydispersity index:	1.27

### Example 3

35.5 kg of the polyhydric dendritic polyether obtained in Example 1 was heated to 80°C and an aqueous solution of KOH was charged in an amount corresponding to 357 g of neat KOH. The reaction mixture was stirred at said temperature for 1 hour, after which the alcoholate of the product obtained in Example 1 was considered to have formed. Full vacuum was then applied and the temperature was gradually increased to 110°C to remove any water present in the alcoholate mixture. 28.8 kg of ethylene oxide was now under pressure and nitrogen atmosphere charged to the reaction mixture during 1.5 hour and the temperature was kept at 110-120°C. The reaction was allowed to continue at 110°C for a further 3 hours after completed feeding of ethylene oxide. The reaction product was then cooled to 80°C and sulphuric acid was added in stoichiometric amounts to previously charged KOH.  $\text{K}_2\text{SO}_4$  precipitated from the solution and was removed by filtration, after which the final product was recovered.

Obtained chain extended dendritic polyether exhibited following properties:

Hydroxyl value, mg KOH/g:	291
Average hydroxyl functionality, eq:	14.1
Peak molecular weight (GPC), g/mole:	2723
Molecular weight (GPC), g/mole:	2575
Nominal molecular weight (GPC), g/mole:	2033
Polydispersity index (PDI):	1.27
Viscosity (25°C, Brookfield), mPas:	9200
Non-volatile content, % by weight:	99.5

#### Example 4

Example 3 was repeated with the difference that 86.5 kg of ethylene oxide was charged instead of 28.8 kg and that the feeding time was 3 hrs instead of 1.5 hr.

Obtained chain extended dendritic polyether exhibited following properties:

Hydroxyl value, mg KOH/g:	150
Average hydroxyl functionality, eq:	10.8
Peak molecular weight (GPC), g/mole:	4052
Molecular weight (GPC), g/mole:	4181
Nominal molecular weight (GPC), g/mole:	3153
Polydispersity index:	1.33
Viscosity (25°C, Brookfield), mPas:	2200
Non-volatile content, % by weight:	99.5

#### Example 5

36.5 kg of the polyhydric dendritic polyether obtained in Example 2 was charged to a reactor and heated to 80°C and an aqueous solution of KOH was charged in an amount corresponding to 450 g of neat KOH. The reaction mixture was stirred at said temperature for 1 hour, after which the alcoholate of the product obtained in Example 1 was considered to have formed. Full vacuum was then applied and the temperature was gradually increased to 110°C to remove any water present in the alcoholate mixture. 28.8 kg of ethylene oxide was now under pressure and nitrogen atmosphere charged to the reaction mixture during 1.5 hour and the temperature was kept at 110-120°C. The reaction was allowed to continue at 110°C for a further 3 hours after completed feeding of ethylene oxide. The reaction product was then cooled to 80°C and sulphuric acid was added in stoichiometric amounts to previously charged

KOH. K<sub>2</sub>SO<sub>4</sub> precipitated from the solution and was removed by filtration, whereafter the final product was recovered.

Obtained chain extended dendritic polyether exhibited following properties:

Hydroxyl value, mg KOH/g:	289
Average hydroxyl functionality, eq:	32.2
Peak molecular weight (GPC), g/mole:	6362
Molecular weight (GPC), g/mole:	5204
Nominal molecular weight (GPC), g/mole:	2690
Polydispersity index:	1.93
Viscosity (25°C, Brookfield), mPas:	22000
Non-volatile content, % by weight:	99.5

#### Example 6

Example 5 was repeated with the difference that 86.5 kg of ethylene oxide was charged instead of 28.8 kg and that the feeding time was 3 hrs instead of 1.5 hr.

Obtained chain extended dendritic polyether exhibited following properties:

Hydroxyl value, mg KOH/g:	149
Average hydroxyl functionality, eq:	18.6
Peak molecular weight (GPC), g/mole:	7001
Molecular weight (GPC), g/mole:	6045
Nominal molecular weight (GPC), g/mole:	2607
Polydispersity index:	2.32
Non-volatile content, % by weight:	99.5

#### Example 7

80.0 g of the chain extended dendritic polyether according to Example 2, 32.1 g of acrylic acid (10% by weight in excess to the stoichiometric ratio) and 115 ml of toluene were at room temperature charged to a reactor. The temperature was raised to 55°C and 1500 ppm of 4-methoxyphenol and 300 ppm of nitrobenzene were added. 1.1 g of methane sulphonic acid was added when a clear solution was obtained. The temperature was now slowly raised to 110°C and maintained to reflux. Air was allowed to bubble through the reaction mixture to avoid gelation. The acid value was after 7 hours 62 mg KOH/g and the reaction was stopped. The reaction mixture was cooled to room temperature and the product filtered through a glass

filtration. The reaction mixture was neutralised to pH 7 with a 4% aqueous solution of NaOH. Separation between the aqueous phase and the organic phase occurred almost instantaneously and the organic phase was washed 3 times with water (product:toluene/water = 2:1). Remaining toluene was finally vaporised at 40°C and < 10 mm Hg for 1 hour and the final product was recovered.

Obtained chain terminated chain extended dendritic polyether (chain extended dendritic polyether acrylate) exhibited following properties:

Final acid value, mg KOH/g:	2.5
Acrylate concentration, mmole/g:	3.2
Peak molecular weight (GPC), g/mole:	4947
Molecular weight (GPC), g/mole:	4125
Nominal molecular weight (GPC), g/mole:	2610
Polydispersity index:	1.58
Viscosity (25°C, 30 s <sup>-1</sup> , Cone and Plate), mPas:	1100
Non-volatile content, % by weight:	95.6

### Example 8

Example 7 was repeated with the difference that the chain extended dendritic polyether of Example 5 was used instead of the chain extended dendritic polyether of Example 3.

Obtained chain terminated chain extended dendritic polyether (chain extended dendritic polyether acrylate) exhibited following properties:

Final acid value, mg KOH/g:	4.2
Acrylate concentration, mmole/g:	4.7
Peak molecular weight (GPC), g/mole:	6783
Molecular weight (GPC), g/mole:	6826
Nominal molecular weight (GPC), g/mole:	3387
Polydispersity index:	2.01
Viscosity (25°C, 30 s <sup>-1</sup> , Cone and Plate), mPas:	2300
Non-volatile content, % by weight:	97

### Example 9

90.0 g of sunflower fatty acid was charged to a reactor equipped with stirrer, water removal trap of Dean-Stark type, cooler, temperature control, electric heater and nitrogen purge. The

fatty acid was during 1 hour heated to 80°C. 200.0 g of the chain extended dendritic polyether of Example 4, 2.9 g of benzoic acid and 21.0 g of xylene were charged to the heated fatty acid. The reaction mixture was now during 1 hour heated to 175°C at which temperature reflux commenced. The reaction was allowed to continue for a further 12 hours. The temperature was gradually increased, to maintain good reflux, until a final reaction temperature of 195°C was reached. Full vacuum was applied, when the reaction mixture had reached an acid value of approx. 7 mg KOH/g, to remove any residual solvent from the reaction mixture. The reaction mixture was then cooled to 50°C and a filtering aid (Celite) was added. Finally, the reaction mixture was passed through a pressurised filter and the final product was obtained.

Obtained chain terminated chain extended dendritic polyether (chain extended dendritic polyether alkyd) exhibited following properties:

Final acid value, mg KOH/g:	6.6
Hydroxyl value, mg KOH/g:	56
Molecular weight (GPC), g/mole:	7667
Nominal molecular weight (GPC), g/mole:	3324
Polydispersity index:	2.31
Viscosity (Brookfield, 23 °C), mPas:	2570
Non-volatile content, % by weight:	99.5

#### Example 10

The chain extended dendritic polyether acrylates obtained in Examples 7 and 8 were mixed with 4% by weight of Irgacure® 500 (photoinitiator, CIBA, Switzerland) and evaluated as clear coatings. The coatings were produced by the K-bar 12 µm on metal plates and passed 6 times under a 80 W/cm mercury bulb lamp in a Wallace Knight Unit. Obtained cured coatings were characterised by pendulum hardness (König pendulum), pencil hardness and Erichsen flexibility. Surface conversion of the double bonds was monitored by FTIR attenuated reflectance (Nicolet Protégé) by monitoring the decrease of the double bond absorbency at 810 cm<sup>-1</sup> and by using the carbonyl peak at 1715 cm<sup>-1</sup> as internal reference.

Crosscut test of coatings cured under the same conditions was done on corona treated polyethylene in order to evaluate the adhesion and ranked as follows:



5: Intact



4



3



2



1



0: Bad

A comparison with a tetrafunctional amine modified polyether (Reference), characterised by a molecular weight of 1000 g/mole and a viscosity of 3 Pa.s at room temperature, was furthermore made. 4-7 times higher molecular weights at lower or similar viscosity and similar acrylate concentrations (approx. 4.0 mmole/g) were obtained with products according to the present invention compared with the reference acrylate. Similar or higher flexibility, higher pendulum hardness, similar or higher chemical resistance and improved adhesion on polyethylene were obtained with products according to Examples 7 and 8 compared to the Reference.

The result of the evaluation is given in Table 1 below.

#### **Example 11**

The chain extended dendritic polyether acrylates obtained in Examples 7 and 8 and the reference mentioned in Example 10 were mixed with an alkoxylated pentaerythritol acrylate (Ebecryl® 40, UCB Chemicals, Belgium) at a weight ratio 50:50. The formulations were cured with 2% Irgacure® 500 (photoinitiator, CIBA, Switzerland) and evaluated, at a filmthickness of 12 µm, as in Example 10.

Higher chemical resistance and improved adhesion is obtained with products according to Examples 7 and 8 compared to the Reference.

The result of the evaluation is given in Table 2 below.

#### **Example 12**

The chain extended dendritic polyether according to example 5 was evaluated as toughener in an anhydride cured epoxy resin.

5 parts and 10 parts, respectively, of the chain extended dendritic polyether according to Example 5 were at room temperature added to and mixed into 100 parts of a bisphenol-A type of epoxy (LY556, Vantico, Switzerland). Opaque solutions were obtained. 90 parts of an anhydride hardnener (HY917, Vantico, Switzerland) and 1 part of an imidazole accelerator (DY070, Vantico, Switzerland) were then mixed with the opaque mixtures and the mixtures became fully transparent.

A reference was also prepared in the same manner as above, with the difference that the chain extended dendritic polyether according to Example 5 was excluded.

The mixtures were subsequently poured into steel moulds with dimensions according to the required specimen size for tensile testing and fracture toughness evaluation. The filled moulds were first degassed in a vacuum oven to remove entrapped air and then cured according to the following curing schedule:

RT => 1.5°C/min => 80°C => 4hrs at 80°C => 1.5°C/min => 140°C => 6hrs at 140°C => -0.3°C/m => RT

The cured specimens were free of defects when demoulded and fully transparent. The cured specimens were then machined to dumb bell shape according to standards for evaluation of tensile properties. Fracture toughness was also evaluated with specimens machined into the shape required for the compact tension test.

Mechanical properties obtained with specimens comprising the chain extended dendritic polyether according to Example 5 and the Reference are given in Table 3 below.

### Example 13

The product of Example 9 was used to prepare a self emulsifying waterborne alkyd emulsion having following composition:

- |                                              |           |
|----------------------------------------------|-----------|
| 1. Product according to Example 9:           | 40 parts  |
| 2. Cobalt drier (Servosyn® WED, 8% Co)*:     | 0.3 parts |
| 3. Zirconium drier (Servosyn® WED, 12% Zr)*: | 0.9 parts |
| 4. Distilled water:                          | 60 parts  |

\* Servo Delden B.V., The Netherlands.

Components 1-3 were mixed by stirring and water was subsequently added. The pH was adjusted to 7 by addition of an aqueous dimethylamino ethanol solution (10%). A translucent emulsion was obtained. The emulsion was after 5 days at 40°C still stable.

Obtained product exhibited following characteristics:

Solid content, % by weight:	41
Viscosity (23°C, 0s <sup>-1</sup> , Cone and Plate), Pa.s:	2.1
Volatile organic content (VOC), %:	0

**Example 14**

The alkyd emulsion prepared in Example 13 was used as a dispersing medium for pigments. A high concentrated pigment paste was prepared by adding, during 20 minutes in a high speed dissolver at 2000 rpm, 70 g of TiO<sub>2</sub> (Kronos® 2310) to 30 g of the alkyd emulsion obtained in Example 13. The pigment paste was after 5 days at 40°C still stable.

Obtained product exhibited following characteristics:

Pigment:resin, weight ratio:	5.8:1
Solid content, % by weight:	82
Viscosity (23°C, 0s <sup>-1</sup> , Cone and Plate), Pa.s:	110
Viscosity (23 °C, 500s <sup>-1</sup> , Cone and Plate), Pa.s:	3.5

**Example 15**

An alkyd/acrylic hybrid emulsion was prepared by mixing, during 20 minutes, 30 parts of the product obtained in Example 13 with 70 parts of an acrylic dispersion (Mowilith® LDM 7451, Perstorp Clariant AB) having a solid content of 47%. Additives or coalescent agents were not used to prepare the hybrid system. The hybrid system was after 5 days at 40°C still stable.

Obtained product exhibited following characteristics:

Solid content, % by weight:	44.9
Volatile organic content (VOC), %	0
Viscosity (23°C, 0s <sup>-1</sup> , Cone and Plate), Pa.s:	10
Viscosity (23 °C, 500s <sup>-1</sup> , Cone and Plate), Pa.s:	0.3

**Example 16**

A waterborne paint formulation based on the alkyd/acrylic hybrid emulsion of Example 15 and the pigment paste of Example 14 was prepared by slowly adding 60 g of said pigment paste to 90 g of said alkyd/acrylic hybrid emulsion. Additives or coalescent agents were not used to prepare the hybrid system. The hybrid emulsion was after 5 days at 40°C still stable.

Obtained product exhibited following characteristics:

Solid content, % by weight:	59
Pigment:resin, weight ratio:	1:1.12

Viscosity (23°C, 0s <sup>-1</sup> , Cone and Plate), Pa.s:	14
Viscosity (23 °C, 500s <sup>-1</sup> , Cone and Plate), Pa.s:	0.55
Volatile organic content (VOC), %:	0

### Example 17

The product of Example 9 was used to water disperse an alkyd resin intended for solvent borne systems and thus not giving a stable emulsion when water dispersed.

A 75% oil length alkyd, based on tall oil fatty acid and pentaerythritol, having a nominal molecular weight of 4793 g/mole and hydroxyl value of 36 mg KOH/g was under stirring mixed with the product of Example 9 at a weight ratio of 2:1. A cloudy highly viscous mixture was obtained. The same dryers as in Example 13 were subsequently added followed by addition of distilled water to a solid content of 50%. Obtained mixture was now stirred for 20 minutes resulting a stable milky emulsion. The emulsion was after 5 days at 40°C still stable.

Obtained product exhibited following characteristics:

Solid content, % by weight:	50
Viscosity (23°C, 0s <sup>-1</sup> , Cone and Plate)*, Pa.s	15
Viscosity (23°C, 500s <sup>-1</sup> )*, Pa.s:	0.55
Volatile organic content (VOC), %:	0

The viscosity (s<sup>-1</sup>, Cone and Plate) as a function of shear rate is given is Graph 1 below.

### Example 18

A waterborne paint formulation based on the alkyd emulsion of Example 17 and the pigment paste prepared of Example 14 was prepared by slowly adding 60 g of said pigment paste to 90 g of said alkyd emulsion. The paint was after 5 days at 40°C still stable.

Obtained product exhibited following characteristics:

Solid content, % by weight:	62.8
Pigment:resin, weight ratio:	1:1.24
Viscosity (23°C, 0s <sup>-1</sup> , Cone and Plate), Pa.s:	20
Viscosity (23°C, 500s <sup>-1</sup> , Cone and Plate), Pa.s:	1.2
Volatile organic content (VOC), %:	0

**Example 19**

100 µm wet films from the formulations of Examples 14-18 were coated on glass panels and dried at 23 ± 2°C and 55 ± 5% relative humidity. The acrylic dispersion (Mowilith® LDM 7451, Perstorp Clariant AB) of Example 15 was used as Reference. The hardness was recorded using a König pendulum and expressed as König seconds.

The result is given in Table 4 below.

**Table 1**

	<b>Example 7</b>	<b>Example 8</b>	<b>Reference</b>
Pendulum hardness, König secs.	75	78	59
Erichsen flexibility, mm	4	4.4	3.2
Acetone double rubs	20	30	30
Pencil hardness	2H	2H	2H
Polyethylene adhesion	5	5	3
Water resistance, 6 hrs. **	3	3	2
Conversion, %	100*	100*	90

\* Double bond peak intensity too low for quantitative measurement, below the sensitivity of the instrument.

\*\* Rank: 5 = No effect, 4=Small blisters, 3=Easy to scratch, 2=Very low scratch resist, 1=Lifting, 0=Highly damaged

**Table 2**

	<b>Example 7</b>	<b>Example 8</b>	<b>Reference</b>
Pendulum hardness, König secs.	88	87	89
Erichsen flexibility, mm	3.9	4	3.4
Acetone double rubs	400	> 500	350
Curl, mm	2.3	1.9	2.3
Polyethylene adhesion	5	5	3
Water resistance, 2 hrs. **	5	5	5
Water resistance, 24 hrs. **	2	4	2
Conversion, %	100*	100*	N.a.

\* Double bond peak intensity too low for quantitative measurement, below the sensitivity of the instrument.

\*\* Rank: 5 = No effect, 4=Small blisters, 3=Easy to scratch, 2=Very low scratch resist, 1=Lifting, 0=Highly damaged

N.a. = Not applicable.

**Table 3**

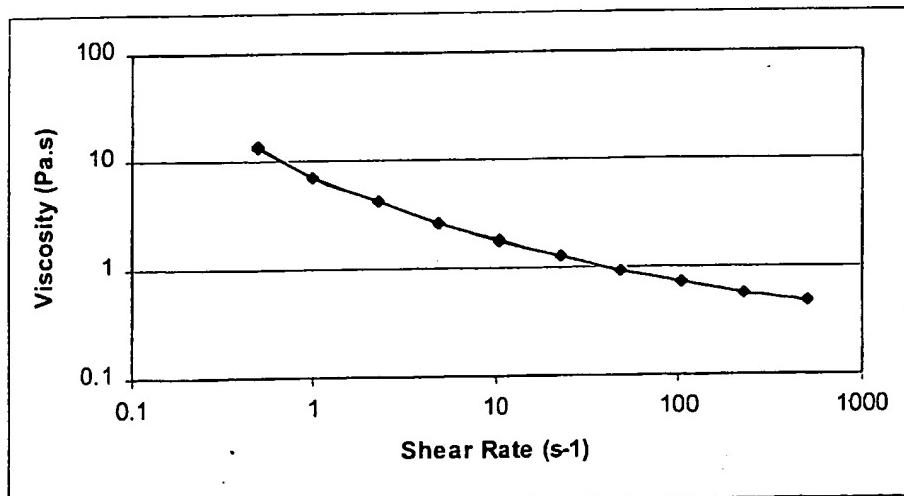
	<b>Example 5 5 pph</b>	<b>Example 5 10 pph</b>	<b>Reference</b>
Tensile Modulus	3.0	2.9	3.1
$\sigma$ Yield, MPa	82.3	89.0	89.7
Strain, %	5.3	8.0	4.6
Critical Stress Intensity Factor, MPa.m $^{1/2}$	0.55	0.60	0.46
Glasstransition temperature, °C	135	130	133

**Table 4**

	<b>Ex. 14</b>	<b>Ex. 15</b>	<b>Ex. 16</b>	<b>Ex. 17</b>	<b>Ex. 18</b>	<b>Ref.</b>
Pendulum hardness - 24 hrs., König secs.	18	10	10	46	32	42
Pendulum hardness - 2 days, König secs.	20	10	10	55	42	48
Pendulum hardness - 5 days, König secs.	24	10	10	57	45	52

**Graph 1**

Viscosity as a function of shear rate for product according to Example 17.



**CLAIMS**

1. A chain extended dendritic polyether comprising a dendritic core polymer and a chain extension bonded to said core polymer, which chain extended dendritic polyether optionally is at least partially chain terminated and/or partially functionalised characterised in, that said core polymer is a polyhydric dendritic polyether and that said chain extension is obtained by addition of at least one alkylene oxide to at least one hydroxyl group in said core polymer at a molar ratio said core polymer to said alkylene oxide of between 1:1 and 1:100, preferably between 1:2 and 1:50.
2. A chain extended dendritic polyether according to Claim 1 characterised in, that said alkylene oxide is ethylene oxide, propylene oxide, 1,3-butylene oxide, 2,4-butylene oxide, cyclohexene oxide, butadiene monoxide, phenylethylene oxide or a mixture of two or more of said alkylene oxides.
3. A chain extended dendritic polyether according to Claim 1 or 2 characterised in, that said polyhydric dendritic polyether is obtained by ring opening addition of at least one oxetane to a di, tri or polyhydric core molecule at a molar ratio yielding a polyhydric dendritic polyether comprising a core molecule and at least one branching generation bonded to at least one hydroxyl group in said di, tri or polyhydric core molecule.
4. A chain extended dendritic polyether according to Claim 3 characterised in, that said di, tri or polyhydric core molecule is a 1, $\omega$ -diol, a 5-hydroxy-1,3-dioxane, a 5-hydroxyalkyl-1,3-dioxane, a 5-alkyl-5-hydroxyalkyl-1,3-dioxane, a 5,5-di(hydroxyalkyl)-1,3-dioxane, a 2-alkyl-1,3-propanediol, a 2,2-dialkyl-1,3-propanediol, a 2-hydroxy-1,3-propanediol, a 2-hydroxy-2-alkyl-1,3-propanediol, a 2-hydroxyalkyl-2-alkyl-1,3-propanediol, a 2,2-di(hydroxyalkyl)-1,3-propanediol or a dimer, trimer or polymer of a said di, tri or polyhydric alcohol.
5. A chain extended dendritic polyether according to Claim 3 or 4 characterised in, that said di, tri or polyhydric core molecule is 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,6-cyclohexanedimethanol, 5,5-dihydroxymethyl-1,3-dioxane, 2-methyl-1,3-propanediol, 2-methyl-2-ethyl-1,3-propanediol, 2-ethyl-2-butyl-1,3-propanediol, neopentyl glycol, dimethylolpropane, 1,1-dimethylolcyclohexane, glycerol, trimethylolethane, trimethylolpropane, diglycerol, ditrimethylolethane, ditrimethylolpropane, pentaerythritol, dipentaerythritol, anhydroenneaheptitol, sorbitol or mannitol.

6. A chain extended dendritic polyether according to Claim 3  
characterised in, that said di, tri or polyhydric core molecule is a reaction product between at least one alkylene oxide and a 1, $\omega$ -diol, a 5-hydroxy-1,3-dioxane, a 5-hydroxyalkyl-1,3-dioxane, a 5-alkyl-5-hydroxyalkyl-1,3-dioxane, a 5,5-di(hydroxyalkyl)-1,3-dioxane, a 2-alkyl-1,3-propanediol, a 2,2-dialkyl-1,3-propanediol, a 2-hydroxy-1,3-propanediol, a 2-hydroxy-2-alkyl-1,3-propanediol, a 2-hydroxyalkyl-2-alkyl-1,3-propanediol, a 2,2-di(hydroxyalkyl)-1,3-propanediol or a dimer, trimer or polymer of a said di, tri or polyhydric alcohol.
7. A chain extended dendritic polyether according to Claim 3 or 6  
characterised in, that said di, tri or polyhydric core molecule is a reaction product between at least one alkylene oxide and 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,6-cyclohexane dimethanol, 5,5-dihydroxymethyl-1,3-dioxane, 2-methyl-1,3-propanediol, 2-methyl-2-ethyl-1,3-propanediol, 2-ethyl-2-butyl-1,3-propanediol, neopentyl glycol, dimethylolpropane, 1,1-dimethylolcyclohexane, glycerol, trimethylolethane, trimethylolpropane, diglycerol, ditrimethylolethane, ditrimethylolpropane, pentaerythritol, dipentaerythritol, anhydroenneaheptitol, sorbitol or mannitol.
8. A chain extended dendritic polyether according to Claim 6 or 7  
characterised in, that said alkylene oxide is ethylene oxide, propylene oxide, 1,3-butylene oxide, 2,4-butylene oxide, cyclohexene oxide, butadiene monoxide and/or phenylethylene oxide.
9. A chain extended dendritic polyether according to any of the Claims 3-8  
characterised in, that said oxetane is a 3-alkyl-3-(hydroxyalkyl)oxetane, a 3,3-di(hydroxyalkyl)oxetane, a 3-alkyl-3-(hydroxyalkoxy)oxetane, a 3-alkyl-3-(hydroxyalkoxyalkyl)oxetane or a dimer, trimer or polymer of a 3-alkyl-3-(hydroxyalkyl)oxetane, a 3,3-di(hydroxyalkyl)oxetane, a 3-alkyl-3-(hydroxyalkoxy)oxetane or a 3-alkyl-3-(hydroxyalkoxyalkyl)oxetane.
10. A chain extended dendritic polyether according to Claim 9  
characterised in, that said oxetane is 3-methyl-3-(hydroxymethyl)oxetane, 3-ethyl-3-(hydroxymethyl)oxetane and/or 3,3-di(hydroxymethyl)oxetane.
11. A chain extended dendritic polyether according to Claim 9 or 10  
characterised in, that said oxetane is an oxetane of trimethylolethane, trimethylolpropane, pentaerythritol, ditrimethylolethane, ditrimethylolpropane or dipentaerythritol.

12. A chain extended dendritic polyether according to any of the Claims 1-11 characterised in, that said dendritic polyether is at least partially chain terminated by addition to said chain extension and/or said core polymer of at least one aliphatic or aromatic saturated or unsaturated carboxylic acid or a corresponding anhydride or halide, aliphatic or aromatic mono or diisocyanate, epoxidised saturated or unsaturated alcohol, allyl or vinyl ether, thiol, glycidyl ether, sulphonate or phosphate.
13. A chain extended dendritic polyether according to any of the Claims 1-12 characterised in, that said dendritic polyether is at least partially functionalised by reaction with at least one allyl halide, such as allyl bromide and/or allyl chloride, and/or at least one epihalohydrin, such as epichlorohydrin and/or epibromohydrin.
14. A chain extended dendritic polyether according to any of the Claim 1-11 characterised in, that said dendritic polyether is at least partially chain terminated by addition to said chain extension and/or said core polymer of acrylic acid, methacrylic acid, crotonic acid, isocrotonic acid or a to a said acid corresponding anhydride or halide.
15. A chain extended dendritic polyether according to any of the Claim 1-11 characterised in, that said dendritic polyether is at least partially chain terminated by addition to said chain extension and/or said core polymer of acetic acid, propionic acid, butyric acid, valeric acid, isobutyric acid, trimethylacetic acid, nonanoic acid, isononanoic acid, 2-ethyl-hexanoic acid, caproic acid, caprylic acid, capric acid, heptanoic acid, benzoic acid, para-tert.butylbenzoic acid, pelargonic acid, lauric acid, myristic acid, palmitic acid, stearic acid, isostearic acid, behenic acid, lignoceric acid, cerotic acid, montanoic acid, abietic acid, sorbinic acid, oleic acid, ricinoleic acid, linoleic acid, linolenic acid, erucic acid, soybean fatty acid, linseed fatty acid, dehydrated castor fatty acid, tall oil fatty acid, tung oil fatty acid, sunflower fatty acid, safflower fatty acid, *o*-phthalic acid, isophthalic acid, terephthalic acid, azeleic acid, adipic acid and/or trimellitic acid or a to a said acid corresponding anhydride.
16. A composition comprising a chain extended dendritic polyether according any of the Claims 1-15 characterised in, that said composition comprises at least 0.1%, such as 0.5-80%, 0.5-50% or 1-25%, by weight of said dendritic polyether.
17. Use of a chain extended dendritic polyether according to any of the Claims 1-15 characterised in, that said chain extended dendritic polyether is used as or utilised in preparation of
  - i) an air drying alkyd resin,

- ii) a 1- or 2-component polyurethane coating or adhesive,
- iii) a saturated or unsaturated polyester,
- iv) a toughening agent for thermosetting resins, such as an epoxy resins, unsaturated polyesters, vinyl esters, polyurethanes, maleimides, cyanate esters, phenolics urea-formaldehyde resins and melamine-formaldehyde resins, and/or composites made therefrom,
- v) a pigment dispersion agent for solvent-free, solventborne and waterborne coatings,
- vi) a water dispersible resin for alkyd emulsions, acrylic dispersions and polyurethane dispersions,
- vii) a dispersing polymer or resin, such as a reactive polymeric surfactant, for non-amphifilic alkyds, polyesters, polyethers and polyurethanes,
- viii) a processing aid for polyolefines and thermoplastics, such as polycarbonates, polyamides, polyester, polyimides and polyurethanes,
- ix) a concrete admixture imparting fluidity to hydraulic compositions, such as cement pastes, mortars or concretes, and/or
- x) a radiation curing coating, printing ink or adhesive.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 03/00117

## A. CLASSIFICATION OF SUBJECT MATTER

**IPC7: C08G 83/00**

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

**IPC7: C08G, C09D, C08L**

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

**SE,DK,FI,NO classes as above**

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

**WPI, EPODOC, DIALOG, CAPLUS**

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Macromolecules, Volume 33, 2000, Ralf Knischka et al, "Functional Poly(ethylene oxide) Multiarm Star Polymers: Core-First Synthesis Using Hyperbranched Polyglycerol Initiators" page 315 - page 320 --	1-2
Y	WO 0056802 A1 (PERSTORP AB), 28 Sept 2000 (28.09.00) --	3-17
Y	Solid State Ionics, Volume 148, 2002, Masayoshi Watanabe et al, "Polymer electrolytes derived from dendritic polyether macromonomers" page 399 - page 404 --	3-17

 Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:	
"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier application or patent but published on or after the international filing date	"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

Date of mailing of the international search report

7 April 2003

09-04-2003

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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 03/00117

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>Macromolecules, Volume 33, 2000,            Alexander Sunder et al, "Hyperbranched            Polyether-Polyols Based on Polyglycerol: Polarity            Design by Block Copolymerization with Propylene            Oxide" page 309 - page 314</p> <p>--</p>	1-2
A	<p>Polymeric materials science and engineering,            Volume 75, 1996, keith w. pollak et al, "Nonionic            Unimolecular Micelles: Poly(ethylene oxide)-coated            dendrimers" page 273 - page 274</p> <p>--</p>	1,2
A	<p>Polymer, Volume 43, 2002, Anna Carlmark et al,            "Atom transfer radical polymerization of methyl            acrylate from a multifunctional initiator at            ambient temperature" page 4237 - page 4242</p> <p>--</p> <p>-----</p>	3-17

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

28/02/03

International application No.

PCT/SE 03/00117

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WO 0056802 A1	28/09/00	AU	4155300 A	09/10/00
		AU	4812199 A	30/12/99
		EP	1187868 A	20/03/02
		SE	514207 C	22/01/01
		SE	9901033 A	24/09/00